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Phosphorus recovery from municipal solid waste incineration fly ash

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ABSTRACT

The potential of phosphorus (P) recycling from municipal solid waste incineration (MSWI) residue is investigated. Vast and ever increasing amounts of incineration residues are produced worldwide; these are an environmental burden, but also a resource, as they are a major sink for the material flows of society. Due to strict environmental regulations, in combination with decreasing landfilling space, the disposal of the MSWI residues is problematic. At the same time, resource scarcity is recognized as a global challenge for the modern world, and even more so for future generations.

This paper reports on the methods and efficiency of P extraction from MSWI fly ash by acid and base leaching and precipitation procedures. Phosphorus extracted from the MSWI residues generated each year could meet 30% of the annual demand for mineral phosphorus fertiliser in Sweden, given a recovery rate of 70% achieved in this initial test.

The phosphorus content of the obtained product is slightly higher than in sewage sludge, but due to the trace metal content it is not acceptable for application to agricultural land in Sweden, whereas application in the rest of the EU would be possible. However, it would be preferable to use the product as a raw material to replace rock phosphate in fertilizer production. Further development is currently underway in relation to procedure optimization, purification of the phosphorus product, and the simultaneous recovery of other resources.

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1. Introduction

Ever since the industrial revolution, perpetually increasing amounts of natural resources have been transferred to the anthropogenic sphere, where they accumulate as waste products or, alternatively, are dissipated into the environment in the form of emissions.

In this study, we particularly recognize the environmental impact caused by the anthropogenic phosphorus (P) cycle and the decreasing reserves of high-quality phosphate rock (Heffer, 2006). The anthropogenic phosphorus cycle is characterized by major diffuse losses, which cause phosphorus transfer from the geosphere to the hydrosphere, consequently leading to eutrophication. Some 27 million ton y^{-1} of phosphorus (as P) is added to agricultural land in the form of fertilizer, while only 3 million ton y^{-1} is consumed by humans through our diet, and the rest is dissipated (van Enk and van der Vee, 2011). This transfer is expected to intensify due to an increase in the global population, the gradual elimination of under-nutrition, and a dietary transition towards higher consumption

of both animal-derived products and of fruit and vegetables in developing countries. Based on these facts, we believe that every opportunity to keep the anthropogenic phosphorus in a closed loop, thereby mitigating the use of phosphorus rock, should be considered.

Landfills are sinks for resources and can potentially be used for resource mining. Incineration is a commonly used method for treatment of waste, before landfilling, to reduce volume and sometimes also for energy recovery. A study of phosphorus flows for the EU27, Japan and for a municipality in Sweden, recently showed that solid waste, and its incineration residues in particular, contain as much phosphorus as does the sewage sludge (Kalmykova and Harder, 2012; Matsubae-Yokoyama et al., 2009; Ott and Rechberger, 2012). Food and food processing wastes is a major source of P in solid waste (4.0 g P/kg TS, total solid). Other sources of P in solid waste are wood, paper and textile (0.2–0.3 g P/kg TS). Separate collection of food waste is implemented only in a few countries worldwide. When implemented, a minor part of the total food and processing waste is separately collected due to both, the low collection rate from households and large non-separated flows from food distribution and retail, restaurants and public institutions (Kalmykova and Harder, 2012). Therefore, solid waste is expected to contain considerable amount of P even in the foreseeable future.

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The municipal solid waste incineration (MSWI) residue offers a relatively homogeneous and concentrated stock for mineral recovery. Metal recovery is currently being investigated, and full-scale plants for Zn recovery are under development in Switzerland (Karlfeldt Fedje et al., 2012; Schlumberger and Buehler, 2012). MSWI residues generally contain lower amounts of phosphorus compared to wastewater sludge, ~0.4% and 2–6% respectively (Karlfeldt Fedje, 2010; Pettersson et al., 2008). On the other hand, large quantities of waste ash and slag are available worldwide. In Sweden alone, the estimated amount of P in MSWI residues is 4400 ton y⁻¹ and in the EU27, the corresponding value is 52,000 ton y⁻¹ (Sverige, 2011; Eurostat, 2011).

Previous studies of phosphorus recovery from waste materials have looked at extraction from sewage sludge (SS), sewage sludge ash (SSA), and chicken manure ash (CMA). The methods used to extract phosphorus from ashes include electro-kinetic (Sturm et al., 2010), thermo-chemical (Adam et al., 2009); bioleaching and accumulation (Zimmermann and Dott, 2009), and wet chemical methods, such as acid leaching (Biplob Kumar Biswas et al., 2009; Donatello et al., 2010) and acid or acid–base leaching with subsequent precipitation (Kaikake et al., 2009; Levlin et al., 2005; Petzet et al., 2011). In this study, the wet chemical methods have been investigated, due to the low efficiency or long processing time required for the other methods. The electro-kinetic method achieved less than 1% recovery, while bioleaching and bioaccumulation requires 11 days for completion, something which could potentially hinder its up-scaling to an industrial facility. In contrast, the acid dissolution–alkali precipitation method could yield 92% P extraction from CMA (Kaikake et al., 2009), the acid leaching of ashes from co-combustion of sewage sludge and wood (Pettersson et al., 2008), and the two-step acid–base leaching of the SSA, showed 50–80% and 60–80% of phosphorus release respectively (Levlin et al., 2005; Petzet et al., 2011).

This paper describes the procedures and results of wet chemical method applications to P recovery from MSWI fly ash. Modified versions of the acid dissolution–alkali precipitation and the two-step acid–base leaching have been applied. The original ash, the intermediate solutions, and the resulting phosphorus products have been analyzed and their possible further uses are discussed.

2. Materials and methods

2.1. Material

A mixture of three electrostatic filter ash samples collected during 24 h and generated during normal circumstances by a mass burn (MB) combustor for incineration of municipal and industrial solid waste, was used in this study. No lime was added for flue gas treatment before the electrostatic filter. The ash is a dry, fine material with particle size in the range 50–950 µm (median 340 µm) and no grinding was required. Material has been dried overnight at 105 °C prior to experiments.

2.2. Analytical methods

The main crystalline compounds in the original ash sample were identified by qualitative X-ray powder diffractometry (XRD), using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a scintillation detector. The measurement was made using a continuous scan in region 10–70° in 2θ with step 0.02° with 1 s measurement time each step. The identification of compounds was carried out using the Joint Committee of Powder Diffraction Standards Database (JCPDS, 2010). The detection limit of this method is about 1% by weight for a certain mineral. In the study of optimal leaching conditions,

the phosphorus in ash leachates was measured by HACH DR/890 colorimeter with the standard PhosVer3 Method. For the subsequent tests, the elemental composition, including phosphorus, of the ash leachates, filtrates and precipitants were analyzed at an accredited lab by the ICP-AES with the reported measurement uncertainties ±10–20%. Carbon, H and N were analyzed by Elementar vario MAX CHN, and Cl by Konelab Aqua 60. When needed during the leaching and recovery experiments, the pH was controlled by a Metrohm SM 702 Titrino. All tests were conducted at room temperature and in triplicates, except for the maximum P leaching experiments that were done in duplicates. All filtration was performed using membrane filters with a 0.45 µm pore diameter. Simulations of the leachates solution chemistry were carried out using CHEAQS Pro software (Verweij, 2012).

2.3. Leaching and recovery experiments

The composition of the ash has important implications for the development of the extraction procedures. The wet chemical methods of extraction are based on the solubility of salts as a function of pH. For solubility of phosphates, see Stumm and Morgan, 1996. For solubility of trace metal's salts, see Drever, 1997. Most metal salts are soluble at acidic pH and have very low solubility at basic pH. Phosphates, on the other hand, are soluble at acidic and AlPO₄ also at basic pH values. Therefore, the leaching of MSWI ash with base could potentially be selective for phosphorus. However, CaHPO₄ and Ca₄H(PO₄)₃ have low solubility at neutral to basic pH values and could potentially inhibit the extraction of phosphorus. As an example, Ca content has been shown to be a limiting factor for P release at basic leaching of SSA (Stendahl and Jafverstrom, 2004). While 90% of P has leached from the SSA with a 3% Ca content, 65% of P has leached from the SSA with an 8% Ca content. Therefore two leaching and recovery processes were tested in this study:

- acidic leaching of the ash, followed by recovery of P from the leachate using sequential precipitation at pH = 3, 4 (Method I);
- acidic leaching of the ash, followed by alkaline leaching of the remaining ash to achieve a P-rich solution (Method II).

The P leaching efficiency, P_{le} , in wt.% is calculated according to

$$P_{leachate}/P_{ash} * 100 = P_{le} \quad (1)$$

where $P_{leachate}$ and P_{ash} refers to the average P amounts given as mg P/kg dry ash in the leachate and in the ash, respectively. Corresponding equations were also used to calculate the leaching efficiencies for the other elements of interest.

The overall recovery efficiency for P (RE_p) is calculated according to

$$M_{p\ 2nd\ prec}/m_{p\ leachate} * 100 = RE_p \quad (2)$$

where $M_{p\ 2nd\ prec}$ is the mass (g) of P found in the 2nd precipitant and $m_{p\ leachate}$ is the mass (g) of P present in 20 mL of the original batch leachate.

The dissolution of the ash matrix (D_{ash}) during leaching is calculated according to

$$1 - (m_{ash\ leach\ orig}/m_{ash}) * 100 = D_{ash} \quad (3)$$

where $m_{ash\ orig}$ is the mass of original ash used and $m_{ash\ leach}$ is the mass of the corresponding ash residue, both calculated on 100% dry ashes.

2.3.1. Recovery Method I – Acidic leaching and precipitation

To begin with, the dissolution step was optimized to obtain maximum P leaching. Factors such as acid concentration and hence the pH, leaching time and sedimentation time were considered to be critical factors effecting P leaching. Hydrochloric acid (HCl) concentrations of 1, 1.5, 2, 2.5 and 3 M, and leaching times of 2, 4 and 24 h were used, while the liquid-to-solid-ratio (L/S) was kept constant at 5 in all leaching experiments. For acid concentrations of 1.5 and 2.5 M, only a 2-h leaching time was tested. The samples were rotated upside-down for the required time in air tight, acid pre-cleaned plastic bottles. Sedimentation times of 5 min and 24 h were tested. The leachates were then filtrated through a 0.45 μm filter and the pH recorded. A flow chart describing the procedure for the optimal acidic leaching followed by acidic precipitation (Method I) is presented in Fig. 1.

Larger amounts of leachate were produced under the identified optimal conditions (100 g of dry ash and 500 mL 2 M HCl i.e. L/S 5). However, due to the large sample volume, decantation was used instead of filtration to separate leachate and ash residue. To obtain the first precipitation, 20 mL of the P rich leachate was titrated with 1 M NaOH at a constant pH = 3.0 for 1 h at a 500 rpm stirring rate. The particles formed during this process were separated by filtration and oven-dried at 50 °C. The resulting filtrate was titrated with 1 M NaOH at a constant pH of 4, for 5 h at a 400 rpm stirring rate. The formed precipitant, i.e. the P product, was separated by filtration and oven-dried at 50 °C.

2.3.2. Recovery Method II – Two step acidic–alkaline leaching

A flow chart which describes the procedure for the acid leaching–alkaline precipitation method is presented in Fig. 1, and is based on the method suggested by Levlin et al. (2005). The samples were rotated upside-down for the required time in air tight acid pre-cleaned plastic bottles. In the first step, the ash was leached for 2 h with 1 M HCl at pH = 4 to release Ca. The remaining solids were separated by filtration and leached in a second step for 4 h with 1 M NaOH at pH interval 11–13. A P-rich solution was obtained after filtration.

3. Results and discussion

3.1. Characteristics of the ash sample

The XRD analyses showed that the dominating crystalline compounds were NaCl and CaSO_4 (Fig. 2). Aluminum was also identified, but not the Iron (Fe). The latter is probably due to the fact that Fe is distributed through several different minerals while the detection limit of the XRD method is 1% by weight for a certain mineral. The prevalent form of phosphorus is likely to be KCaPO_4 . The contents of major and minor elements in the studied ash are given in Table 1.

The high content of Ca (14%) in the MSWI ash sample could make the basic leaching of P inefficient. In addition, the contents of Fe (2%) and Al (3%) are several times higher than the P content (0.6%) (Table 1). Acidic leaching would result in a higher extraction of P, whereas basic leaching could potentially result in a cleaner final product since few heavy metals are dissolved at alkaline pH values. Both approaches are tested in this study, with a preliminary step aimed at the reduction of Ca, Fe and Al. For this reason, Method I, the acidic leaching and precipitation, employs an intermediate precipitation step at pH 3 to remove precipitated Al and Fe salts. In particular, Kaikake et al. (2009) has shown for the CMA that precipitation at pH 3 removed 98% of Fe (and 7% of P). Iron and Al are unwanted in the final solid product because their phosphates have low solubility and plant availability. In Method II, Ca is removed in the preliminary acidic leaching (washing) in order to enable subsequent basic leaching of phosphorus.

3.2. Method I – Leaching and recovery of P by acidic leaching and precipitation

3.2.1. Optimal leaching conditions for P

Leaching using 1 M HCl released low fractions of P, while both 2 M HCl and 3 M HCl more or less released all P originally present in the ash, independently of leaching time used (Fig. 3 and Table 2). To minimize the consumption of virgin chemicals (HCl) and to

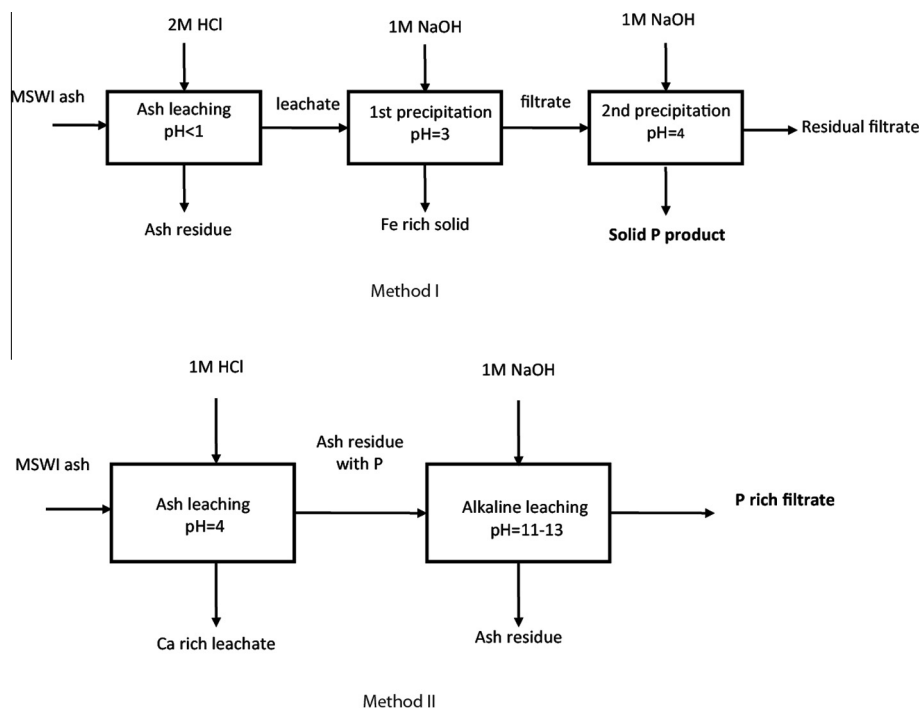


Fig. 1. Applied methods: Method I – acidic leaching and precipitation (above); Method II – two step acidic–alkaline leaching.

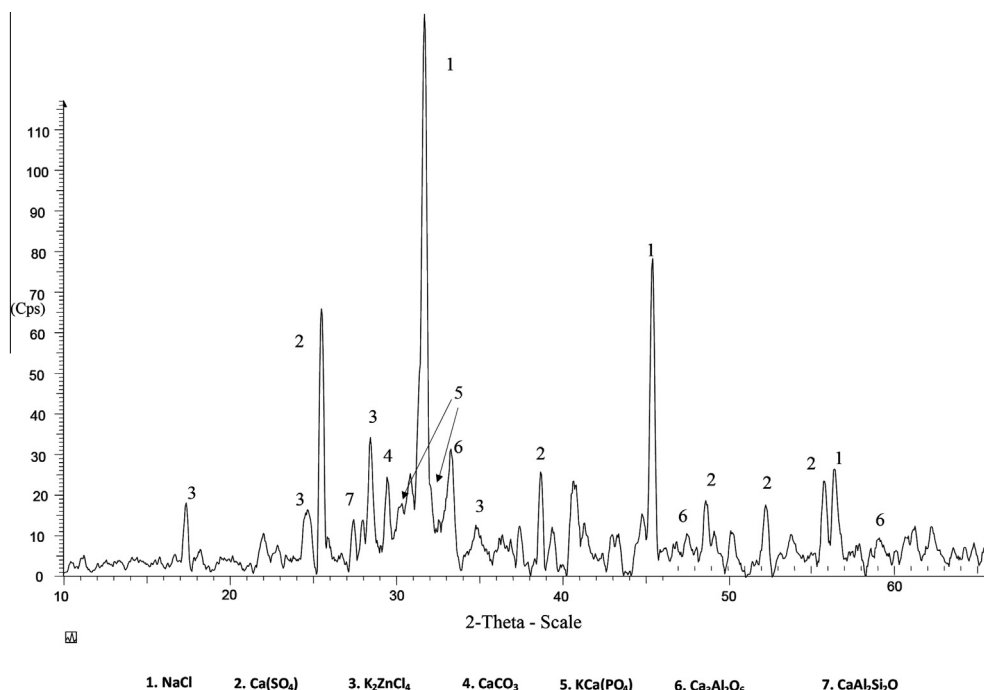


Fig. 2. The main crystalline compounds in the original ash sample as identified by qualitative X-ray powder diffractometry (XRD).

Table 1
Composition of the MSWI fly ash.

| | | | | | | | | | | | |
|-------------------------|----|-----|-----|------|------|-----|------|-----|------|------|----|
| Major elements g/kg | Al | Ca | Fe | K | Mg | Na | Si | Ti | P | S | Zn |
| | 32 | 141 | 19 | 54 | 13 | 58 | 45 | 10 | 5.9 | 65 | 37 |
| Minor elements mg/kg | Ag | As | B | Ba | Be | Cd | Co | Cr | Cu | Hg | |
| | 32 | 460 | 300 | 400 | <2.5 | 270 | 12 | 490 | 2000 | 0.51 | |
| | Mo | Mn | Ni | Pb | Sb | Se | Sn | V | | | |
| | 36 | 810 | 100 | 4600 | 1900 | <10 | 1200 | 49 | | | |

reach a time and energy efficient P recovery process the optimal conditions for maximum P release were chosen to 2 h leaching with 2 M HCl (L/S = 5). In addition, the dissolution of the ash matrix itself (D_{ash}) was lower after 2 h leaching compared to 24 h leaching (30 wt.% and 40 wt.%, respectively) using 2 M HCl. The solutions used in the subsequent P precipitation experiments were obtained under these conditions. In the 2-h experiment 1.5 M and 2.5 M HCl were also tested and yielded 90% and 100% respectively (results are not shown in Fig. 3 or in the Table 2 because no 4-h and 24-h experiments were done for these concentrations).

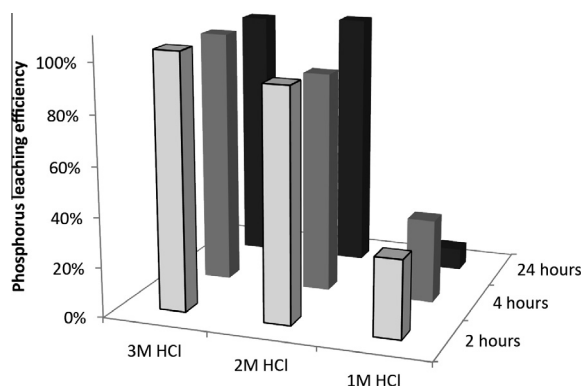


Fig. 3. Phosphorus release from the MSWI ash as a function of reaction time and HCl concentration.

It was noted that ash leachates obtained at short reaction times of 2 and 4 h, and with acid concentrations of 1.5–2 M, became a gel within 24 h if the leachates were separated from the ash residue immediately. In contrast, sedimentation for 24 h before separation of the leachate and ash residue prevented the gel formation and all subsequent samples were therefore allowed to sediment for 24 h before filtration.

Sedimentation decreased the aqueous Si concentration by a factor of 3, whereas the decrease in P concentration was negligible. The possible mechanism of this phenomenon is the reaction of silicate and hydrogen ions to form silicic acid in acidic solutions (pH was <0.9 in all the leachates that turned into gel). Silicic acid is inherently unstable, and will condense and grow to form silica gel (Hauser, 1955). Silicic acid formation is prevented by sedimentation, due to the release of alkaline compounds from the ash residue, such as CaCO_3 , which in turn increases the pH.

Table 2
Average concentrations of P (mg/L) detected in leachates using different HCl concentrations (1, 2 and 3 M) and leaching times (2, 4 and 24 h).

| Leaching time (h) | 3 M HCl Leachate (mg/L P) | 2 M HCl Leachate (mg/L P) | 1 M HCl Leachate (mg/L P) |
|----------------------|------------------------------|------------------------------|------------------------------|
| 2 | 60.9 ± 0.06 | 55.0 ± 0.05 | 18.5 ± 0.00 |
| 4 | 60.5 ± 0.04 | 52.7 ± 0.03 | 19.8 ± 0.03 |
| 24 | 60.6 ± 0.03 | 61.3 ± 0.1 | 5.1 ± 0.02 |

Table 3

Leaching efficiencies (wt.%) [Eq. (1)] and distribution of elements between the Method I steps. From the 20 mL of P rich batch leachate that was used in the recovery process 0.8 g (precipitant 1) and 0.31 g (precipitant 2) dry solid products were generated, respectively.

| | (1) Leaching efficiency (wt.%) | (2) m_0 i.e. mass in the leachate ^a (mg) | Fraction of (2) found in 1st precipitant ^b (wt.%) | Fraction of (2) found in 2nd precipitant ^c (wt.%) | Fraction of (2) found in residual filtrate ^d (wt.%) | Mass balances ^e |
|----|--------------------------------|---|--|--|--|----------------------------|
| P | 93 | 22 | 27 | 72 | 2.9 | 100 |
| Al | 48 | 92 | 12 | 45 | 9.9 | 67 |
| As | 100 | 1.9 | 27 | 68 | 4.3 | 100 |
| Ca | 30 | 280 | 9.0 | 1.8 | 49 | 60 |
| Cd | 98 | 1.1 | 9.9 | 3.3 | 56 | 69 |
| Co | 46 | 0.04 | 11 | <D.L. | 72 | – |
| Cr | 39 | 0.8 | 15 | 98 | 1.5 | 100 |
| Cu | 95 | 7.6 | 7.4 | 7.7 | 42 | 57 |
| Fe | 42 | 32 | 19 | 63 | 16 | 98 |
| Mg | 80 | 42 | 9.3 | 1.9 | 47 | 58 |
| Mn | 80 | 2.6 | 8.7 | 2.9 | 53 | 65 |
| Ni | 42 | 0.17 | 12 | 9.9 | <D.L. | – |
| Pb | 100 | 20 | 12 | 12 | 51 | 75 |
| Sn | 46 | 2.2 | 44 | 80 | 1.0 | 100 |
| V | 100 | 0.12 | 20 | 86 | 0.85 | 100 |
| Zn | 69 | 130 | 11 | 3.9 | 55 | 70 |

<D.L. below detection limit.

^a $C_{orig} \text{ leachate} * V_{leachate \text{ used}} = m_0$, where $C_{orig} \text{ leachate}$ refers to the concentration of metal M or P in the original leachate using the optimal leaching parameters, $V_{leachate \text{ used}}$ refers to the volume of the original leachate used in recovery Method I and m_0 refers to the mass found in $V_{leachate \text{ used}}$.

^b Fraction of element M detected in 1st precipitant = $m_{1st \text{ prec}}/m_0 * 100$.

^c Fraction of element M detected in 2nd precipitant = $m_{2nd \text{ prec}}/m_0 * 100$.

^d Fraction of element M detected in the residue leachate = $m_{res \text{ filtrate}}/m_0 * 100$.

^e Mass balance (%) = $(m_{1st \text{ prec}} + m_{2nd \text{ prec}} + m_{res \text{ filtrate}})/m_0 * 100$, where m_x refers to the mass of each element detected in precipitants 1 and 2 and in the residual filtrate, respectively.

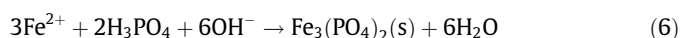
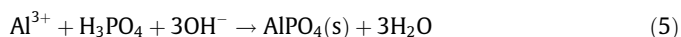
3.2.2. Recovery of P from the leachate

The recovery of P from the leachate was divided into two precipitation steps. The aim of the first step was to remove Fe and Al, while the second produced the final solid P product. The fraction and the mass of the elements leached from the ash, and the distribution of elements in the two steps are presented in Table 3. Phosphorus was effectively leached from the ash by 93%, however also As and metals such as Cd, Cu, Pb and Zn were released by 70–100%. Despite this, only a minor proportion of the metals accumulated in the solid products (precipitants), due to the low pH during the precipitation steps (pH = 3–4), at which most metals are found as free ions in the solution. The major part of the metals was found in a small volume of phosphorus-poor residual filtrate that has been investigated for metals recovery in another study (Modin and Karlfeldt Fedje, 2012).

According to the XRD analysis (Fig. 2) Al is present as low soluble silicate and oxide, while Ca is present as more easily soluble compounds (CaSO_4 and CaCO_3), if in an acidic environment. Therefore, Ca is expected to be released to a higher extent compared to Al during the acidic leaching. This was however not found (30% and 48%, respectively), which is likely due to the high Ca concentration in the leachate decreasing the rate of further Ca release. It should be noted that twice higher release of P (93%) is obtained by the acidic leaching compared to the Al (48%) and Fe (42%) and three times higher than the Ca (30%). In such a way, Fe/P and Al/P molar ratios decrease, which is important for potential use of the resulting product as a fertiliser because iron and aluminum phosphates may have low solubility in soils (depending on the pH of the soil). Whether or not the first precipitation step aimed at Fe and Al removal was necessary is debatable, as considerable fraction of P (27%) was also removed. The alternative of precipitation in one step would result in an Fe concentration of 16 g kg^{-1} , i.e. three times lower than the Fe content of the sewage sludge obtained from chemical precipitation, which is considered to be a relatively good fertilizing product (Eriksson, 2001). Calculation of the solution chemistry with CHEAQS Pro for the two precipitation steps has been conducted. The solid phases $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3(\text{H}_2\text{O})_5$ and $\text{Fe}(\text{II})_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$ has been formed at both pH 3 and 4; other

solids at pH = 4 were AlPO_4 , and $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. The residual filtrate contained 2.9% of the initial leachate P content and no further precipitation steps are required. The final product (2nd precipitant) contained 72% of the initial leachate P content and 30 g kg^{-1} P, which is slightly higher than the average of 27 g kg^{-1} P in 48 sewage sludge samples studied in Sweden (Eriksson, 2001).

Eqs. (4)–(7) below describe the probable mechanism of P precipitation reactions through the two precipitation steps. Equilibrium distributions of phosphorus species as a function of pH are well known (Beukenkamp et al., 1954). At the initial pH = 0.1 in the leachate, the dominant specie is H_3PO_4 . As the pH rises, H_3PO_4 begins to transform into H_2PO_4^- (Eq. 4). At the pH = 3–4 $\text{Al}_3(\text{PO}_4)_2$, $\text{Fe}_3(\text{PO}_4)_2$ and AlPO_4 are formed (Eq. (5)). The H_2PO_4^- reaches its peak when the pH rises to 4 and HPO_4^{2-} begins to form (Eq. (7)). Even after pH = 4 is reached during the second precipitation step, the addition of more NaOH is required to keep the pH constant, which indicates the presence of reactions that consume hydroxide ions. It is likely that these are caused by the production of solid phosphate compounds (Eqs. (8)–(10)), as there are large amounts of e.g. Fe, Mg and Ca in the 2nd precipitation.



The overall efficiency of phosphorus recovery (RE_p) from MSWI ash is about 70 wt.%. The recovery is lower than the 92% obtained for the CMA (Kaikake et al., 2009) and within the range of recovery

Table 4

Compositions of the MSWI ash and other ashes used for wet chemical extraction of phosphorus.

| g/kg | Studied MSWI ash | Sewage sludge ash ^a (SSA) | Chicken manure ash ^b (CMA) | Co-combustion of sewage sludge and wood ^c |
|------|------------------|--------------------------------------|---------------------------------------|--|
| Al | 32 | 218 | – | 36–210 |
| Ca | 141 | 49 | 72 | 40–380 |
| Fe | 19 | 83 | 5.0 | 21–190 |
| Mg | 13 | 6.0 | 22 | 7.0–28 |
| Si | 45 | 94 | – | 11–560 |
| P | 5.9 | 81 | 85 | 17–66 |
| Cr | 0.49 | 0.14 | 0.03 | – |
| Cu | 2.0 | 0.44 | 0.27 | – |
| Zn | 37 | – | 1.6 | – |
| Pb | 4.6 | 0.02 | 0.01 | – |
| Cd | 0.07 | – | – | – |

“–” No value was provided.

^a Levlin et al. (2005).^b Kaikake et al. (2009).^c Pettersson et al. (2008).**Table 5**

Leaching efficiencies (wt.%) [Eq. (1)] of selected metals and P in the acid washing step at pH = 4.

| Element | Al | Ca | Fe | K | Mg | Na | P | S | Si | | | | |
|----------------------------|----|----|-----|-----|----|----|----|----|----|----|----|----|----|
| Leaching efficiency (wt.%) | 4 | 9 | 3 | 100 | 32 | 94 | <1 | <1 | <1 | | | | |
| Element | Ag | Ba | Cd | Co | Cr | Cu | Mo | Mn | Ni | Pb | Sn | Ti | Zn |
| Leaching efficiency (wt.%) | 2 | <1 | 100 | 33 | 3 | 4 | 2 | 19 | 27 | 29 | 1 | <1 | 56 |

obtained for different batches of the ash through co-combustion of the sewage sludge and wood (Pettersson et al., 2008). Under the same experimental conditions, Pettersson et al. have obtained higher P release from Al-rich ashes compared to Fe-rich ashes (75–95% and 50–65% respectively), while no trend has been reported for the Ca content. Composition of the studied ash in comparison to other ashes used for wet chemical extraction of phosphorus is presented in Table 4.

3.3. Method II – Two step acidic-alkaline leaching

The first step of Extraction Method II is acidic leaching of the ash (washing) at pH = 4, to remove Ca and enable effective leaching of the phosphorus in the next basic leaching step. As expected, almost no phosphorus was released but also only 9% of the Ca (Table 5). Therefore, the Ca content in the ash remains high, at 13%, something which could inhibit the release of phosphorus. Elements present as chlorides, such as Na and K, were released in high amounts, >90%, and metals like Cd and Zn were also leached at >50% (Table 5). Nonetheless, the alkaline dissolution of P from the treated ash was tested at several pH values between 11 and 13. As expected the metal release was low at these pH values but unfortunately also the P release (Table 6). The highest dissolution of P was obtained at pH = 12, but still less than 0.1% was released. At pH = 12, metal phosphates are soluble except from calcium phosphates, why it is likely that P is precipitated as calcium phosphate. Therefore, several Ca leaching steps would be needed,

Table 6Trace element loads from 22 kg P ha⁻¹ application of the P product and limits for trace metal loads from sewage sludge application to agricultural land.

| Trace elements (g ha ⁻¹) | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|--------------------------------------|------|------|------|------|------|------|------|
| Phosphorus product | 50 | 1030 | 800 | <0.5 | 23 | 3400 | 6600 |
| Swedish thresholds ^a | 0.75 | 40 | 300 | 1.5 | 25 | 25 | 600 |
| EU thresholds ^b | 50 | 3500 | 7500 | 100 | 3000 | 4000 | 7500 |

^a Swedish EPA (1994).^b EU Council (2001).

requiring larger volumes of acid. In further studies, the newly published method for pre-concentration of alkaline soluble aluminum phosphate will be tested (Petzet et al., 2011). Application of a series acid washing steps at pH = 3–3.5 applied to the SSA with high Al and Ca content was proven to improve consequent alkaline recovery of P from 20% to 67%. Considerable part of contaminants is removed by the first washing step, in particular 100% of Cd, 56% of Zn and 29% of Pb (Table 5). As shown in Table 6, the product obtained by the Method I exceeds the Swedish threshold for trace metals loads to agricultural land for these particular metals. However, their separation from the P-rich material in the Method II could potentially yield a more pure and suitable for agriculture product.

3.4. The purity and usages of the phosphorus product

The composition of the phosphorus product obtained by Method I is presented in Fig. 4. The P accounts for 3w% (dry weight) of the final product, calculated as elemental P, and its content is magnified 5 times compared to the ash.

Commercial mineral fertilizers contain 2.6–20 wt.% of elemental P, depending on sector of application (Yara, 2012). The obtained P product contains 3% P, which is higher than in NPK mineral fertiliser and in the sewage sludge (both 2.7% P). However, the trace element content is much higher than in the sludge and the fertiliser, which prevents the application of P product to agricultural land. Table 7 shows the load of Cd, Cr, Cu, Hg, Ni and Pb, assuming the P product application of 22 kg P ha⁻¹ (average P application in Sweden). All trace elements except Hg and Ni exceed the Swedish limits for metal load through sludge application (Swedish EPA, 1994), while no element exceeds the corresponding EU limits (EU Council, 2001).

In order to avoid any contamination of agricultural land with trace metals, it is preferable for the P product to be used as a secondary resource and substitute virgin phosphate ore in the conventional mineral fertiliser production. Phosphate ores are divided into three quality categories: low-grade (up to 3 wt.% P), intermediate-grade (4–5 wt.% P), and high-grade (6–8 wt.% P). As a result of high-grade phosphate ores becoming scarce, the utilization of low-grade phosphate sources will become increasingly important.

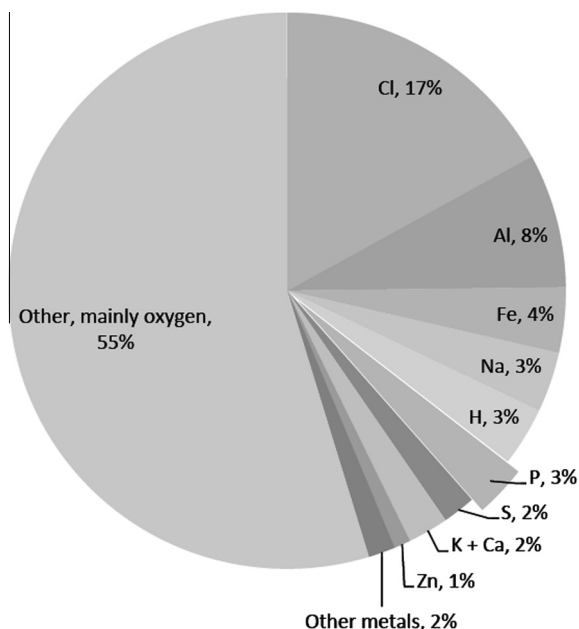


Fig. 4. Composition of the phosphorus product, wt.%. Other metals include Pb, Sn, As, Mg, Cr, Cu, Ti, Sb, V, Mn, Ba, Cd, Ni, Mo, Be and Co.

Table 7
Composition (wt.%) of low-grade phosphate ores compared to the obtained P product.

| | Low grade ore (Iran) ^a | Low grade ore (Turkey) ^b | Phosphorus product from MSWI ash |
|----|-----------------------------------|-------------------------------------|----------------------------------|
| P | 2.2 | 2.4 | 3.0 |
| Ca | 34.6 | 36.6 | 9.5 |
| Al | 1.3 | 0.6 | 7.8 |
| Fe | 1.6 | 0.7 | 15 |
| Mg | 0.3 | 0.8 | 3.8 |

^a Keleş et al. (2010).

^b Mohammadkhani et al. (2011).

Examples of low-grade phosphate ore composition are given in Table 7. No information could be found for trace metal content of the low-grade phosphate ore, as the standard analysis method used by the industry (X-ray fluorescence of selected oxides) does not include trace metals. The P content in the obtained product is 25–30% higher than in the low grade ore.

An important issue in the overall P recovery process is how to treat the residual filtrate and the first precipitation product, as these contain high concentrations of Al, Cu, Mg and Zn. It would be possible to recover these valuable metals as well. For instance, Karlfeldt-Fedje, 2011 states that Cu can be recovered (>90%) from MSWI fly ash leachates through the use of solvent extraction reagents based on oximes. In the future method development two alternatives will be tested: extraction of metals from the residual filtrate and extraction of metals from the ash leachate prior to the phosphorus extraction. Copper extraction from the residual filtrate has already been tested in another study (Modin and Karlfeldt Fedje, 2012).

Solid waste is and will remain a major sink for phosphorus and incineration of solid waste is increasing worldwide. There are several EU legislation acts that divert biodegradable waste, which is also the most P-rich waste type, from landfilling. In particular, the EU Landfill Directive 1999/31/EC obliges member states to reduce the amount of biodegradable waste they place in landfill to 35% of 1995 levels by 2016. In addition, the Animal By-products Regulation (EC) No. 1774/2002 prohibits the feeding of food waste

to animals (EU Council, 2002). Therefore, the incineration of waste and of biodegradable waste in particular, will probably increase in the EU, resulting in larger amounts of phosphorus being found in the MSWI ash.

While phosphorus content is considerably higher in the SSA and CMA, then in the MSWI ash method development for P recycling from MSWI residues is important. Recycling of P from MSWI residues would provide an alternative P resource and improve resilience of the food supply chain by contributing to diverse fertilizer supply.

Based on the 70% P recovery efficiency obtained in this study, 30% of the annual demand for mineral fertilisers in Sweden can be met by the MSWI residues. In 2008, the mineral fertiliser consumption in the EU was 1600 thousand tons P_2O_5 (i.e. 400 thousand tons P). The recovery potential from MSWI ash for the EU is 10%. It should be noted, however, that of the waste incinerated in the EU27, 85% relates to the EU15 countries and the expected built up of the incineration capacity in the new member states will increase amounts of the MSWI residues (Eurostat, 2011).

4. Conclusions

The recovery of P from MSWI fly ash with acidic leaching and precipitation (Method I) and acidic and alkaline leaching (Method II) was investigated in this study. Method I resulted in a recovery of 70% of P content of the ash and the final product contains about 3% P, which is slightly higher than the content of sewage sludge and the low grade phosphate ore. However, the trace metal content limits direct application of this product on agricultural land. It is suggested that the P product is used as a secondary resource for phosphates production, thereby mitigating the use of this non-renewable mineral resource. The method is currently optimized by complementing the P recovery with extraction of metals, and, usage of industrial liquid wastes instead of chemicals and reduction of materials requirements.

Method II resulted in <1% P recovery. The low efficiency is due to the high Ca content of the ash. In further studies, the method will be modified to include a pre-concentration step that reduces Ca content but increases alkaline soluble P. Our results suggest that potentially more pure P product can be obtained by the Method II.

The majority of the world's population live in cities, and solid waste and MSWI residues serve as a sink for urban material flows. In this paper, the potential for mining of P and other resources from MSWI residues has been proved and may be a viable way to meet the increasing demand for resources.

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